T_C suppression in Pr-doped 123-systems: Hole clustering

V. Daadmehr [a,b,*], M.D. Niry [a] and A.T. Rezakhani [c]

[a]*Magnetic and Superconductivity Research Lab, Department of Physics, Iran University of Science and Technology, P.O. Box 16844, Tehran, Iran*

[b]*Magnetic and Superconductivity Research Lab, Department of Physics, Al.Zahra University, Tehran, Iran*

[c]*Department of Physics, Sharif University of Technology, P.O. Box 11365-9161, Tehran, Iran*

Abstract

Doping Pr in 123-systems gives rise to some anomalies, such as T_C suppression. Here, we show that a modification of hole localization theory based on a geometrical modeling by band percolation theory can put forward a good explanations for T_C suppression for whole range of Pr-doping value. In this model the central effect of hole clustering is introduced. Also we have provided some experimental evidences which manifest an agreement between simulation based on hole clustering effect and the experimental data.

Key words: Effects of crystal defects, Transport properties, Y-based cuprates, Hole Localization, Hole Clustering
PACS: 74.62.Dh, 74.25.Fy, 74.72.Bk

1 Introduction

Pr substitutions and its effects on suppression of superconductivity, pinning effect, critical current density (J_C), and other transportation properties in $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (GdPr-123) compounds are among the most interesting subjects in High-Temperature Superconductors (HTSC). The series of $RBa_2Cu_3O_{7-\delta}$ compounds, where R is Y or another rare-earth element except cerium (Ce), praseodymium (Pr), promethium (Pm) and terbium (Tb)

---

* Corresponding author.
    Email address: daadmehr@iust.ac.ir (M.D. Niry).

are metallic and superconducting, with critical temperatures (T_C) that range from 90 to 94 K [1]. These compounds commonly have an orthorhombic layered perovskite-like structure, containing CuO_2 planes within which there are mobile holes that are believed to play role in superconductivity [2]. However the Pr-123 systems has orthorhombic phase structure but it is not a superconductor [1]. Some theoretical models such as, hole filling [3,4], pair breaking [5,6], and localized holes [7,8,9] have been presented to explain the suppression of T_C and superconducting-insulator transition in these compounds. Recently, some groups have reported observation of superconductivity in Pr-123 systems [10]. Blackstead et al. [11] have claimed that mis-substitution of Pr in RPr-123 causes the suppression of superconductivity. In our previous work [12], it has been shown that in spite of the substitution of Pr ion in the rare-earth site, superconductivity is suppressed in GdPr-123 compounds. Researchers have tried to explain this effect by some mechanisms such as hole filling, hybridization, mis-substitution, hole localization [13]. Although, the hole filling, hybridization of Pr $4f$ and O $2p$, and mis-substitution cannot explain completely T_C suppression effect [13], the hole localization is a good base for theoretical explanation of this effect [7,8,14]. In addition, we note that the hole localization have a good agreement with experimental data for lower Pr-doping values [14].

The hole concentration on CuO_2 planes decreases by increasing Pr-doping value in these compounds [1,14]. As well, oxygen deficiency effect in these samples results in decrease in hole concentration [12]. Indeed, it has been shown that there is a correlation between Pr-doping value (x) and oxygen deficiency (δ) [15]. Moreover, there are some dopants such as Ca and Sr which give rise to an increase of hole concentration in CuO_2 planes, which instead results to an increase in T_C. Obviously, the localization model can justify the suppression of T_C in lower values of Pr-doping and it cannot explain other ranges of Pr-doping values, and then need to be corrected.

In this paper, we investigate the behavior of hole concentration in CuO_2 planes in 123-systems for higher Pr-doping values wherein phase transition occurs. This phenomena subject can be related to Coulomb repulsion of localized holes, the collective behavior of Pr ions and clustering effects of Pr-doping on CuO_2 planes in these systems. Here, we try to find a good agreement experimental data and hole localization and, also, hole collective effect of Pr in 123-system for the range of x from 0 to x_C, where superconductivity completely suppress. Beyond this critical value of doping, the system experiences a transition to the normal sate. in this case, however, full analysis of the system requires a 3D percolation modeling.

Our investigation, in this paper, is based upon geometrical considerations. By using concept of band percolation we have introduced notion of hole clustering and hole trapping by which we have modified the effects of localization. In this way, it has been shown that one obtains a good agreement between experimental data and hole collective effects, and also these effects can be extended to full range of Pr-doping.
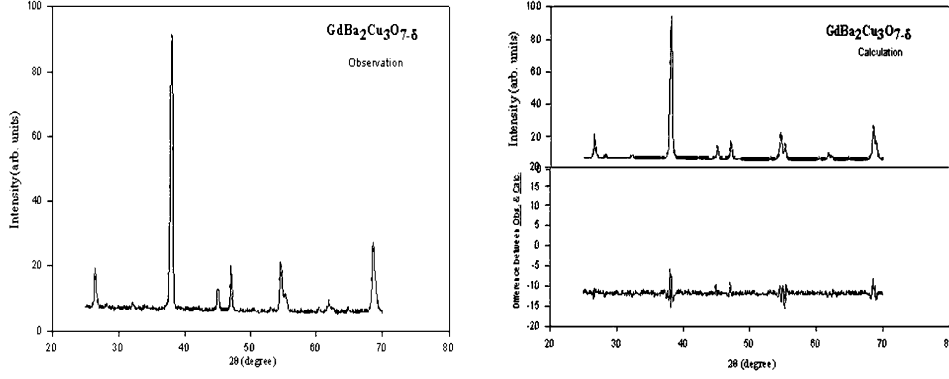
Fig. 1. XRD patterns; experimental (left), Ritveld analysis (upper right), Difference between experimental and Ritveld analysis(lower right).

2 Experimental Details

Single-phase polycrystalline $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples, with $0 < x < 1$ stoichiometry have been prepared by standard solid-state reaction technique. The mixture of Gd_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO powder with 99.9% purity have been calcined at $840\,^{\circ}C$ in air atmosphere for 24 h. The calcination were repeated twice with intermediate grinding. The compounds were then pressed into pellets and sintered in oxygen atmosphere at $930\,^{\circ}C$ for 36 h. To get a sample containing predominately orthorhombic structure we oxygenated it in $650\,^{\circ}C$ for a 1 h period, so that ($\delta \approx 0.15$). Indeed, the preparation procedure is similar to the one of our previous reports [12].

The sintered samples were characterized by powder X-ray diffraction (XRD) using $CoK\alpha$ radiation and scanning electron microscopy (SEM) experiments. The resistivity measurements were carried out by standard ac four-probe method, with 10 mA ac current and frequency of 33 Hz using PAR-124 Lock-in amplifier. The temperature measurements were made by a Lake Shore-330 temperature controller with a Pt resistor and a GaAs diode. The temperature in the range of $300 - 10$ K with 0.10 K accuracy was provided by helium closed-cycle refrigerator.

3 Results and Discussion

3.1 Theories

Orthorhombic structure phase of RPr-123 for Pr-doped value ($0 < x < 1$) was constructed by standard solid state reaction method. Ritveld analysis of XRD patterns for our samples shows in Fig. 1 that predominately phase of our samples is orthorhombic. The lattice parameters, in average, are $a = 3.84, b =$

$3.89, c = 11.69 A°$ Furthermore, it is shown that the volume of unit cell increase by Pr-doping, without any change in phase of the structure. This may be due to Pr ion size which is greater than Gd ion size [1,16,17].

The electrical resistivity of several samples have been shown in Fig. 2. As is seen in this figure, by Pr-doping the critical temperature, T_C, suppresses, and also the normal resistivity increase. Figure. 3 shows suppression of normalized
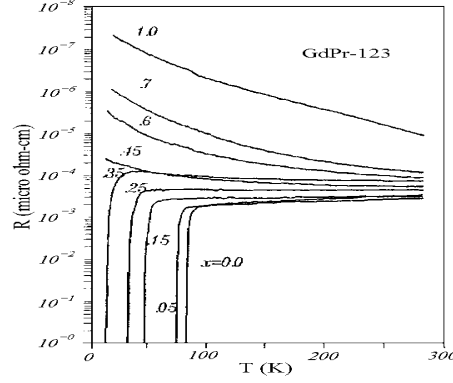

Fig. 2. The electrical resistivity of GdPr-123 versus temperature for different values of oxygen deficiency [1,22].
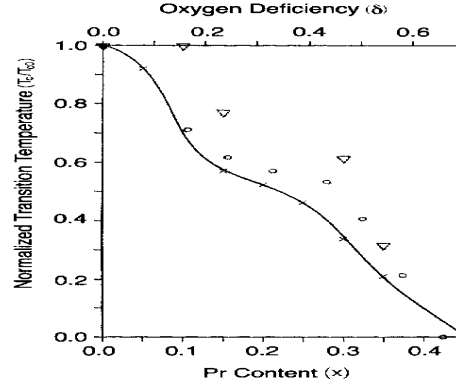

Fig. 3. The critical temperature of GdPr-123 versus Pr-doping value and oxygen deficiency δ [1]. Here, T_{C0} is the transition temperature when $(x = 0)$ and $(\delta = 0)$.
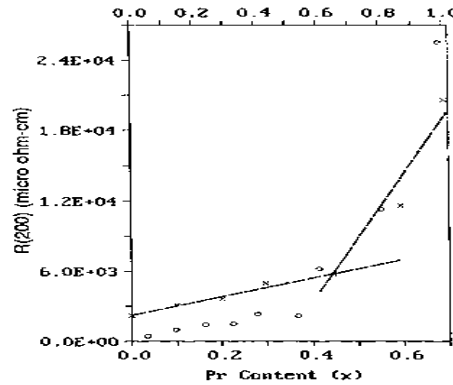

Fig. 4. The electrical resistivity of GdPr-123 versus Pr-doping value [1,22].

4

transition temperature versus Pr-doping value (x) [1]. It is emphasized that, there are two distinct regime; normal and superconductivity, when Pr-doping value, x, changes. Figure 4 illustrates implicity these two regimes, which are separated by the critical value $x_C = 0.45$ for GdPr-123.

In addition, there are several anomalies appeared by Pr-doping, for instance, increase of normal resistivity, no effect on Pinning energy of vortices in vortex dynamics, and also no effect on critical current density J_C [1].

There are some theories to explain Pr anomalies in 123-systems, which also propose some explanations for T_C suppression in 123-systems. There are listed in the following.

3.1.1 Hole Filling

In this mechanism, it is considered that the valance of Pr is significantly greater than +3. This, in turn, results to reduction of hole concentration in the CuO_2 planes [1,3,4,12,18]. However, the results of Hall effect of measurements [3], magnetic susceptibility [3,19], and some others [1,12] turned out inconsistent with some spectroscopic data [13,20].

3.1.2 Pair Breaking

Strong exchange coupling of the Pr $4f$ moments with the spins of the holes in CuO_2 planes results to magnetic pair breaking [5,6,21], It has been known that some rare-earth elements such as Gd and Sm have greater $4f$ moments, however, they do not result to suppression of superconductivity [1].

3.1.3 Mis-substitution

In 123-systems, Pr ions occupy Ba sites instead of Gd position [11]. However, by extended X-ray absorption fine structure, it has been shown that Pr does not substitute for Ba in Pr-123 Compounds in amounts greater than 1% [28,32]. In addition, more recently, it has been observed that Pr/Ba substitution in $Gd(Ba_{2-x}Pr_x)Cu_3O_{7-\delta}$ compounds does not affect its superconductivity [10].

3.1.4 Hole Localization

Hole localization is based on strong hybridization between the Pr localized $4f$ electron and the valance band states that are associated with CuO_2 planes. The mobile hole on the O $2p_\sigma$ state tends to be in localized in O $2p_\pi$ state. Thus, the localized hole cannot move, and gets immobile on CuO_2 planes. As a result, the concentration of mobile holes on CuO_2 planes decreases. On the

5

other word, the hole localization occurs when two R sites adjacent to a CuO_2 planes are occupied by Pr ions. Then Pr-doping can decrease hole concentration on CuO_2 planes, and substantially, T_C is suppressed. Fehrenbacher and Rice (FR) [8] by Hartree calculations, it has been shown that there are only two stable electronic configurations in R-123 systems: i) all holes in a CuO_2 plane are in the Cu^{+3} oxidation state, or exactly, in hybridized Cu $3d$ - O $2p_\sigma$ orbital, and ii) all hole in a CuO_2 plane are in the R^{+4} oxidation state, or exactly, in hybridized R $4f$ - O $2p_\pi$ orbital. There is a small energy difference between Pr^{3+} $4f$ level and the Fermi energy E_F which makes the hole transmission possible. This mechanism provides a satisfactory explanation for Pr effects and insulating nature of $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ [14,21].

3.1.5   Hole Clustering

Here, we show that an alternative mechanism, which is a modification of the hole localization, is also possible. In each superconducting cell, hole concentration decreases when Pr ions substitute for Y(Gd) [1,16]. By increasing Pr-doping value, the probability of that the insulator cells are near some others increases. In this way, some insulator clusters may be formed. The holes trapped inside such these clusters become immobile, and subsequently the hole concentration effectively reduces. Moreover, we believe that when a (nearly) closed belt of such insulator cells is formed, the holes trapped inside get immobile and effectively reduce the hole concentration. This event is similar to the case in which all inside cells have Pr impurities.
In the following sub section, we provide a geometrical background, based upon band percolation theory, for modeling hole localization and hole clustering effects.

3.2   Band Percolation modeling in 123-systems

In this part, we consider some assumptions on the base of which we establish a 2D band percolation model for random distribution of Pr within CuO_2 superconductive planes [25,26]. The main reason for dimensionally 2 for percolation model is that 123-systems are highly anisotropic so that the anisotropy parameter (which is relate to the effective mass tensor) ,γ, ranges from 7 to 50 [31]. Our assumptions are as follow:

(1) In the absence of Pr, to have superconductivity we need at least a CuO2 cell with local hole concentration of 0.25 [29].

(2) An oxygen ion acts as a hole trap in a CuO_2 plane when its two neigh-

boring R sites are both occupied by Pr ions.

(3) Such oxygen ions, irrespective of that they are trapping holes, are inaccessible to mobile holes. In this way, they can be regarded as point defects [14].

(4) Two basic units merge to form a single superconducting region when they are adjacent to each other, sharing two Cu ions and one oxygen ion when they are separated by a non-superconducting layer.

(5) Tendency of R and Pr ions to make a separate structural phase in CuO_2 planes increases by increasing R ion size, so that large ions tend to make more compact larger clusters [16,17,27]. So only for some rare-earth elements like Gd or Y the distribution of Pr position in superconducting CuO_2 planes is uniform random [28].

Validity of the above mentioned assumptions have been discussed in [14] and the references there in. Therefore, CuO_2 planes are made up of two distinct parts: i) S(superconducting)-cells: these are defect free CuO_2 cells which have been considered by the assumption 1 as superconducting. According to the assumption 2, when such these cells get adjacent to each other a superconducting cluster is formed. ii) N(normal)-cells: these are cells in which Pr ions substitute for Gd or Y ions. Also, by combination of N-cells a N-cluster is formed.

By the assumptions 1-4, it is concluded that the probability for that an oxygen ion on a CuO_2 plane have two Pr ions in its neighbored (in plane of R ions) is x^2. By considering that there are 4 nearest neighbors for any site, and provided the oxygen entraps one hole, mobile hole concentration in CuO_2 planes is as follows.

$$n_{mh} = 0.25 - 2x^2 \tag{1}$$

This relation presents a good approximation for hole concentration on CuO_2 plane for lower doping values, x, however, for other values there is not such agreement [14]. The experimental results for Y-123 and Gd-123 systems have been shown in Fig. 5. However, a point, here, is worth noting. In Fig. 5, apparently the experimental data show a less hole concentration. Indeed, as we have explained in Appendix, this effect is due to existence of N-clusters in the system. If we make a simulation and calculate the n_{mh} only on the basis of above Assumptions, we will find the mobile hole concentration only $n_{mh}(x) > 0.15$ with a good approximation (Fig. 5). The Coulomb repulsion between the localized holes tries to prevent localization of holes after the value of Pr-doping approaches $n_{mh}(x) \approx 0.15$. The effects of hole localization
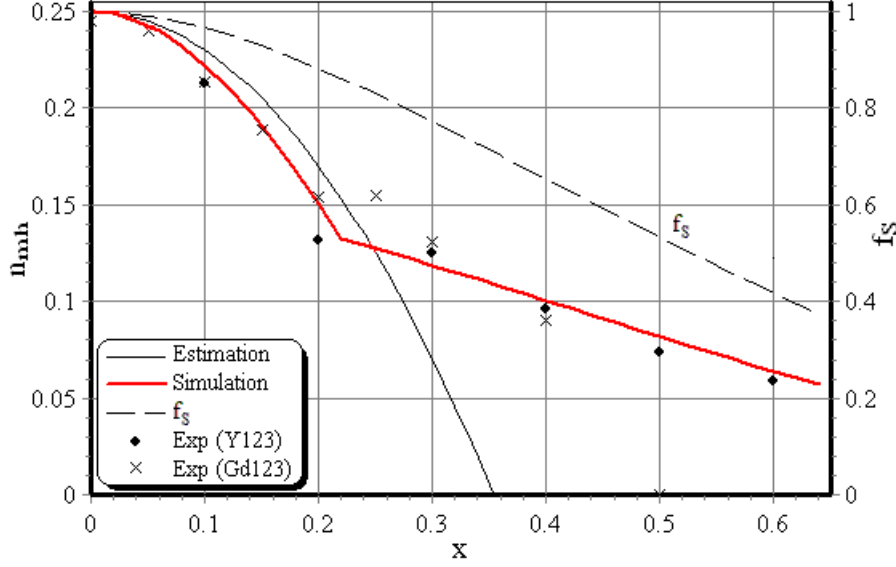
Fig. 5. Mean field approximation hole localization obtained form Eq. 1 (thin solid curve), the simulation result (thick solid curve), and experimental result for Gd-123 and Y-123 systems [24,30]. The dashed curve (measured by the right axis) shows fraction of S-clusters (f_S).

descend after this point. In this stage, the size of normal clusters increases by increasing x. The two phase behavior illustrated in Fig. 5, is similar to the phase transition from ortho. 1 to ortho. 2 observed in behavior of T_C in terms of oxygen deficiency in 123-systems [12]. When Pr-doping value is small, it is
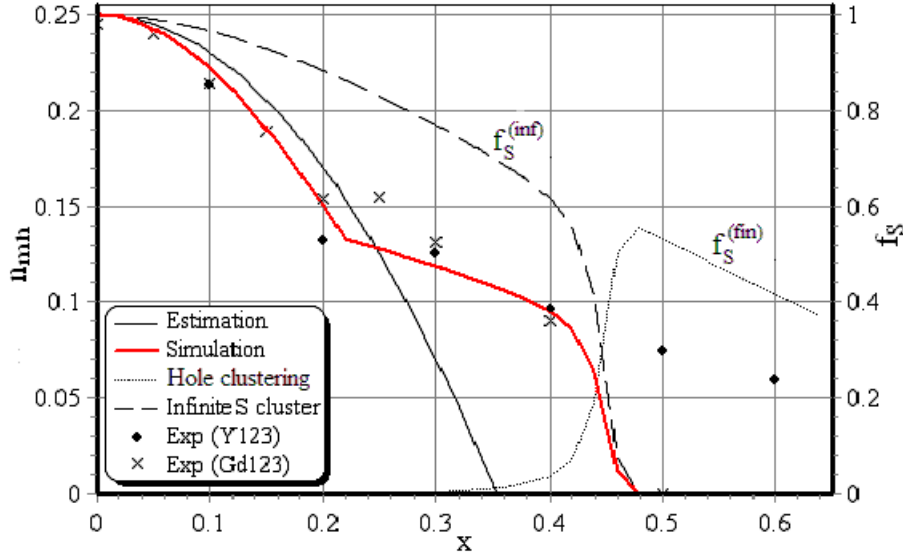

Fig. 6. Hole concentration vs. Pr-doping value, obtained by including hole clustering effect. In $x \approx 0.45$, hole concentration experiences a falloff (thick solid curve). Fraction of infinite S-clusters is shown by the dotted line, and is measured by the right axis.

8

natural that the size of N-clusters are small so that effectively no S-cluster can be present inside N-clusters. By increasing x, the size of N-clusters grows so that it is likely now that some S-clusters get trapped inside N-clusters. In this case, the effective value of hole concentration decreases. Another case, also, may happen. It is possible that the formed belt of N-clusters is not closed. However, when the separation of the two ends of such a belt is small in our investigation, by a good approximation, it can be considered closed. In other words, we assume that a nearly closed belt of insulator cells is taken to be closed. Therefore, such these belts exclude all the holes within. Both of the cases cause some mobile holes get caught inside a region bounded with N-clusters, and thus the contribution of mobile holes in conductivity decreases. When Pr-doping tends to the critical value (x_C) this effect takes place very fast, and we expect to see a phase transition near the percolation threshold (Fig. 6). In this region, as is evident from Fig. 6, as small change of x value gives rise to a considerable change in amount of mobile hole concentration. Decrease of the mobile hole concentration can be attributed to the decrease of the size of infinite S-clusters in our percolation model. Figure 6 contains the experimental result for Y-123 and Gd-123 systems.

4   Conclusion

In this work, we want to explain T_C suppression in 123-systems based on a geometrical modeling. To this aim, some HTSC samples of Gd-123 with dominant orthorhombic phase, for different doping values $0 < x < 1$, have been prepared by solid state reaction technique. Then we have characterized the samples by XRD and Ritveld analysis. By making some assumption supported with band percolation theory, we have investigated suppression of superconductivity and behavior of hole concentration on CuO_2 planes in relation of pr-doping. It has been shown that in low x values, the obtained hole concentration, after an important correction, show a good agreement with experiment. By increasing the doping value, the effect of Coulomb repulsion between trapped holes become more important so that it can compete with hole localization effect, and subsequently, limits it. Finally, it has been obtained that in high values of Pr-doping hole clustering is the dominant effect in explanation of special behavior of n_{mh}, T_C suppression, and phase transition versus x.

A   Appendix

To compare the experimental result of hole concentration based on Hall effect with the accepted definition for $n_{mh}^{(S)}$ of S-clusters in CuO_2 planes [18], defined
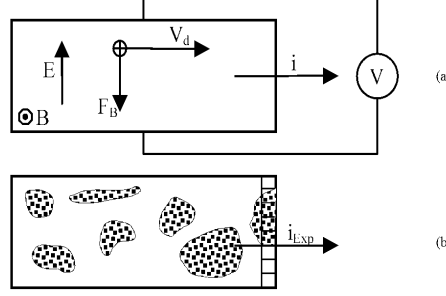
9

Fig. A.1. (a) Hall effect setup for a pure metal. (b) Surface of N-clusters, in super-conductivity planes, is avoided by current.

as

$$n_{mh}^{(S)} = \frac{N_{mh}}{V_S} = \frac{N_{mh}}{V.f_S} \tag{A.1}$$

one must take the measurement mechanism of hole concentration into account. I fact, in Hall effect measurements to find carrier concentration it is implicity assumed that the sample is a pure metal (Fig. A.1). Thus, the following relation for carrier concentration is obtained:

$$n = \frac{Bi}{etV} \tag{A.2}$$

However, in our experiments the processed samples are granular. By Atomic Force Microscopy (AFM) imaging, or other relevant techniques, and using metal-insulator-metal (M-I-M) models the parameters for no-granular single crystal are obtained [23]. Yet, even after this correction, the effect of existence of N-cluster are ignored. This simply means that the actual current measured in experiment is less than the value obtained when the whole compound pure isotropic metal. Thus, to enter this effect into play (Fig. A.1), the current i should be considered as

$$i_{Exp} = i.f_S \tag{A.3}$$

equation (A.2) and (A.3), now, give

$$n = \frac{Bi_{Exp}/f_S}{etV} \tag{A.4}$$

This is, the fraction of S-clusters, f_S, should be multiplied by n_{mh} to give the correct experimental value:

$$n_{mh} = n_{mh}^{(Exp)}/f_S \tag{A.5}$$

References

[1] M. Akhavan, Physica B 321 (2002) 265.

[2] Y. Tokura, J.B. Torrance, T.C. Huang, A.I. Nazzai, Phys. Rev. B 38 (1988) 7156 .

[3] A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe, T. Yamada, Phys. Rev. B 38 (1988) 2910.

[4] A.P. Gonacalves, I.C. Santos, E.B. Lopes, R.T. Henruques, A. Almeida, Phys. Rev. B 37 (1988) 7476.

[5] A. Kebede, C.S Jee, J. Schwelger, J.E. Crow, T. Mihalision, G.H. Myer, R.E. Salomon, P. Schlohmann, M.V. Kuric, S.H. Bloom, R.P. Guertin, Phys. Rev. B 40 (1989) 4453.

[6] J.J. Neumeier, T. Bernholm, M.B. Maple, I.K. Schuller, Phys. Rev. Lett. 63 (1989) 2516.

[7] X.X. Tang, A. Manthiram, J.B. Goodenough, Physica C 161 (1989) 574.

[8] R. Fehrenbacher, T.M. Rice, Phys. Rev. Lett. 79 (1993) 3471.

[9] M. Lee, M.L. Stutzman, Y. Suzuki, and T.H. Geballe. Phys. Rev. B 54 (1996) 3776.

[10] M. R. Mohammadizadeh, M. Akhavan, Phys. Rev. B 68 (2003) 104516.

[11] H.A. Blackstead, J.D. Dow, D.B. Chisey, J.S. Horwitz, M.A. Black, P.J. McGinn, A.E. Klunzinger, D.B. Pulling, Phys. Rev. B 54 (1996) 6122.

[12] H. Khosroabadi, V. Daadmehr, M. Akhavan, Mod. Phys. Lett. B 16 (2002) 943.

[13] H.B. Radosky, J. Mater., Res. 7 (1992) 1917.

[14] M. Muroi, R. Street, Physica C 301 (1998) 277.

[15] V. Daadmehr and M. Akhavan, Phys. Stat. Sol. (a) 193 (2002) 153.

[16] M. Muroi, R. Street, Physica C 228 (1994) 216.

[17] X. J. Yunhui, GCPD e.V. 5 Sep. 1999.

[18] M. Muroi, R. Street, Physica C 216 (1993) 345.

[19] B. Okai, M. Kosuge, H. Nozaki, K. Takahashi and M. Obum, Jpn. J. Appl. Phys. 27 (1988) L41.

[20] J. Fink, N. Nucker, H. Romberg, M. Alexander, M.B. Maple, J.J. Neumeier and J.W. Allen, Phys. Rev. B 42 (1990) 4823.

[21] M.B. Maple, B.W. Lee, J.J. Neumeier, G. Nieva, L.M. Paulius, C.L. Seaman, J. All. Compou., 181 (1992) 135.

[22] Z. Yamani, M. Akhavan, Physica C 268 (1996) 78.

[23] D. Toker, D. Azulay, N. Shimoni, I. Balberg, and O. Millo, Phys. Rev. B 68 (2003) 1403.

[24] M.R. Mohammadizadeh, M. Akhavan, Supercond. Sci. Technol. 16 (2003) 1216.

[25] D. Stauffer, A. Aharony, Introduction to Percolation Theory, (Taylor & Francis, Washington, DC, 1992).

[26] J. Hoshen, R. Kopelman, Phys. Rev. B14 (1976) 3438.

[27] S.K. Malik, C.V. Tomy, P. Bhargva, Phys. Rev. B 44 (1991) 7042.

[28] C.H. Booth, F. Bridges, J.B Byce, T. Claeson, Z.X. Zhao, P. Cervantes, Phys. Rev. B 49 (1994) 3432.

[29] K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, S. Uchida, Phys. Rev. B 46 (1992) 5833.

[30] W.H. Li, K.C. Lee, H.C. Ku, J. Appl. Phys. 81 (1997) 4237.

[31] M. Tinkhham, Introduction to superconductivity, (McGraw-Hill, New York, 1996).

[32] V.G. Harris, D.J. Fatemi, V.M. Browning, M.S. Osofsky, and T.A. Vanderah, J. Appl. Phys. 83 (1998) 6783.